International
Fertilizer Industry
Association

ISMA* Technical Conference

Orlando, Florida, USA
23-27 October 1978

In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).

International Fertilizer Industry Association - Secretariat: 28 rue Marbeuf - 75008 Paris - France
Tel. +33 1 53 93 05 00 - Fax +33 1 53 93 05 45/47 - ifa@fertilizer.org - www.fertilizer.org

PILOT- AND DEMONSTRATION-SCALE DEVELOPMENTS IN PRODUCTION OF AMMONIUM PHOSPHATE-BASED FERTILIZERS USING THE PIPE AND PIPE-CROSS REACTORS

By

B. R. Parker, M. M. Norton, I. W. McCamy,
and D. G. Salladay

Tennessee Valley Authority
National Fertilizer Development Center
Muscle Shoals, Alabama 35660
UNITED STATES OF AMERICA

Paper to be presented at the 1978 International Superphosphate and Compound Manufacturer's Association Limited Technical/Economic Conference in Orlando, Florida, October 22-27, 1978

PILOT- AND DEMONSTRATION-SCALE DEVELOPMENTS IN PRODUCTION OF AMMONIUM PHOSPHATE-BASED FERTILIZERS USING THE PIPE AND PIPE-CROSS REACTORS

By

B. R. Parker, M. M. Norton, I. W. McCamy,
and D. G. Salladay

Tennessee Valley Authority
National Fertilizer Development Center
Muscle Shoals, Alabama 35660
UNITED STATES OF AMERICA

ABSTRACT

Ammonium phosphates produced by the reaction of ammonia with phosphoric acid have been the leading phosphatic fertilizers produced in the United States since 1968. Most of the processes for production of ammonium phosphates use a preneutralizer tank as a reaction vessel prior to the material's being solidified into its final useful form.

In 1973, the Tennessee Valley Authority (TVA) began operation of a demonstration-scale plant that used a simple pipe reactor as a reaction vessel in the production of granular ammonium phosphates containing about 20% of the phosphate content as polyphosphate from a melt which was essentially anhydrous as discharged from the reactor. The viability of this process has been amply proved by the production of such grades as 11-55-0, 28-28-0 and 35-17-0. Pilot-plant work since that time has further refined and simplified this process and has proved its reliability.

In 1974, TVA began pilot-plant tests of a modified pipe reactor in which sulfuric acid was added in some tests in addition to phosphoric acid and ammonia. This reactor, in fact a pipe-cross reactor, has been used very successfully in the production of several grades of NP and NPK granular fertilizers. The most desirable process conditions were defined as the following grades were produced without drying: 12-48-0, 10-40-10, 6-24-24, 13-13-13, 20-10-10, 17-17-17, 33-11-0, and 18-46-0.

This work with the pipe-cross reactor has determined that it operates more smoothly with less scale buildup inside the reaction tube when the melt or slurry temperature is maintained either below 300°F (149°C) or above 400°F (204°C). The degree of scale buildup inside the reaction tube is related to the source of the phosphoric acid. The addition of sulfuric acid to the pipe-cross reactor was most effective in reducing scale buildup when melt or slurry temperatures were above 400°F (204°C). In addition to the work at TVA, at least two other companies have developed processes that utilize compact pipe or nozzle-type reaction systems to produce solid fertilizers.

PILOT- AND DEMONSTRATION-SCALE DEVELOPMENTS IN PRODUCTION OF AMMONIUM PHOSPHATE-BASED FERTILIZERS USING THE PIPE AND PIPE-CROSS REACTORS

Introduction

Ammonium phosphates produced by the reaction of ammonia with phosphoric acid have been the leading phosphatic fertilizers produced in the United States since 1968. For more than 15 years, monoammonium phosphate (MAP) and diammonium phosphate (DAP) have been produced in processes using preneutralizer tanks. These tanks are usually constructed of stainless steel or of mild steel with a lining of acid brick. A plant may have either a single preneutralizer tank or several tanks in series, but in either case, the moisture content of the slurry produced must be high (usually between 15 and 30%) so that the slurry can be pumped with a conventional centrifugal pump and uniformly distributed in a granulator. Because of this high moisture content, the granulator product must be dried.

The following operating problems have been reported by companies that produce MAP and DAP in processes using preneutralizer tanks:

1. Difficulty in pumping and metering the hot slurry from the preneutralizer.
2. Foaming and boiling over of the slurry in the preneutralizer.
3. Difficulty in controlling the slurry level in the preneutralizer.
4. Plugging of the ammonia sparger and poor ammonia distribution in the preneutralizer.
5. Scarcity and high price of fuel needed for drying the product.

Several processes have been developed in which a melt or slurry is produced with a very low moisture content compared with slurries with a relatively high moisture content produced in a preneutralizer. One of the first melt-type processes for NP and NPK fertilizers was a modification of a nitric phosphate process in which supplemental phosphoric acid was sometimes added. This process produced a comparatively dilute slurry. This slurry was concentrated in a fuel-fired, high-temperature rotary evaporator and then granulated in a pugmill with potash, other fertilizer salts, and recycle. This modified nitric phosphate process was developed by TVA in pilot-plant work conducted from 1947 to 1949 (1). Although no dryer was required, there was no relative energy savings because of the high energy requirements of the evaporator. When a small plant was later built to use this process, a conventional dryer was used in the operation to allow more flexibility in formulations. In later work by Norsk-Hydro, a slurry produced by a nitric phosphate-type reaction was concentrated by evaporation and prilled with and without addition of other materials. Their prilled NP and NPK products did not require drying and had very good physical properties.

In later pilot-plant work, TVA developed a process for producing NP and NPK granular fertilizers in which the heat generated by the chemical reactions in a small-volume reaction tube (a pipe reactor) is used effectively to evaporate large quantities of water. S. A. Cros of Spain (2) and Consolidated Fertilizers Limited of Australia (3) have also developed processes that utilize compact pipe or nozzle-type reaction systems to produce granular fertilizers. Information concerning TVA pilot-plant studies of this process was presented at the Technical Conference of the International Superphosphate and Compound Manufacturer's Association, Limited (ISMA), at Sandefjord, Norway, in 1970 (4) and it was published in 1972 (5). This process, which includes a pipe reactor and a pugmill granulator, was put into operation by TVA in December 1973 in a demonstration-scale plant (11-18 mt/hr.) at the National Fertilizer Development Center, Muscle Shoals, Alabama (6). Additional pilot-plant work and process improvements have been made so that operation of the demonstration-scale plant to produce 11-55-0, 28-28-0, and 35-17-0 grades is now routine. TVA has also conducted pilot-plant tests to study the pipe-reactor process using a more versatile rotary drum granulator. Several NP and NPK grades have been produced with this modified process using a preneutralizer, and MAP has been produced both with and without the preneutralizer. Urea was used as a source of supplemental nitrogen in some grades.

Since 1974, TVA has done considerable developmental work on a process which uses a modified pipe reactor (a pipe-cross reactor). The first pipe-cross reactor, which was installed in a commercial fertilizer plant in Palmyra, Missouri, has been used successfully in the production of several NP and NPK grades that required little or no drying (7, 8, 9, 10). In addition to the reduced drying requirements of the product, large amounts of sulfuric acid can also be fed to the process using the pipe-cross reactor. Several pipe-cross reactors are now in commercial operation, and several other installations are planned. TVA is continuing pilot-plant studies of the pipe-cross reactor process to further define process variables and operating conditions necessary to produce additional grades. In these studies, both gaseous and liquid ammonia have been used as feeds to the pipe-cross reactor, and several MAP sulfate grades have been produced. DAP was produced recently both with and without sulfuric acid being added to the pipe-cross reactor, and three urea-ammonium phosphate (UAP) grades have been produced with urea added to the process either as a melt or a solid.

Following are descriptions of TVA processes that use either the pipe reactor or pipe-cross reactor in the production of granular fertilizer. In all of these processes, the chemical reaction is confined to the small volume of the reaction tube and the heat generated is very effective in evaporating large quantities of water thus producing a melt or slurry much lower in moisture content than a slurry produced only in a preneutralizer.

Pipe-Reactor/Pugmill Process

A flow diagram of the pipe-reactor/pugmill process used in a TVA demonstration-scale plant is shown in Figure 1. Merchant-grade (52-54% P_2O_5) wet-process phosphoric acid is metered to a Hastelloy G spray reactor where it reacts with excess ammonia from the pipe reactor. A side stream of the partially reacted acid from the spray reactor is metered to one branch of a 6-inch (15.2 cm) pipe tee on a pipe reactor that is 10 feet long (3.05 m) and made of Schedule 40 Type 316L stainless steel pipe.

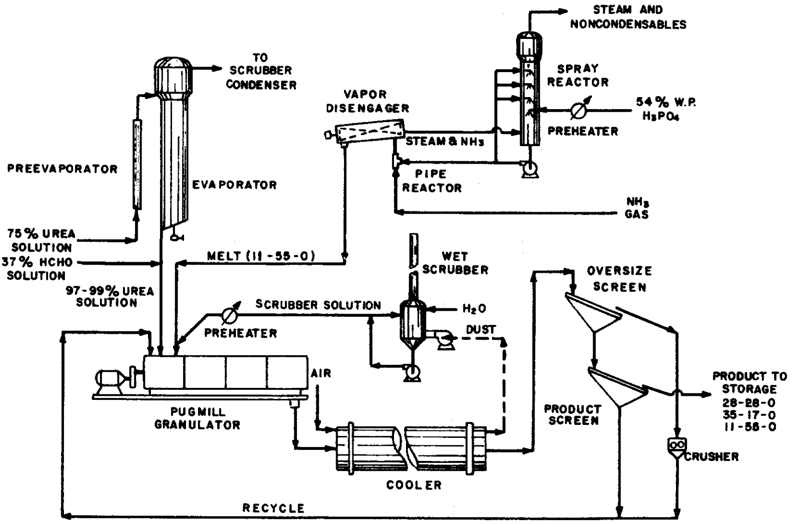


Figure 1. Pipe-Reactor/Pugmill Process

Gaseous anhydrous ammonia is metered to the other branch of the tee. The temperature in the pipe is 400° to 450°F (204°-232°C), so free water and some combined water are evolved and an essentially anhydrous melt containing 15 to 30% polyphosphate is produced. The pipe-reactor melt enters a vapor disengager (see Fig. 2) where helical rotary blades spread the melt to facilitate removal of water vapor (steam) and free ammonia and thus compact and defoam the melt. The melt flows by gravity down a short heated chute from the disengager to a double-shaft pugmill.

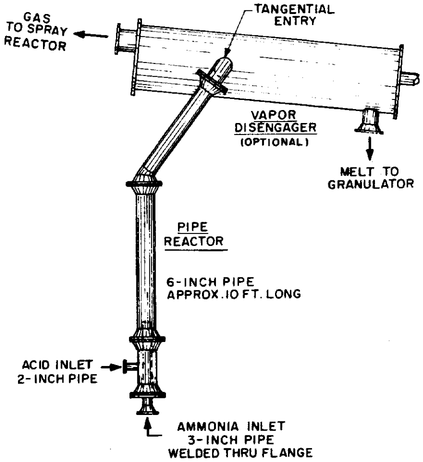


Figure 2. Pipe Reactor and Vapor Disengager

Recycle is fed to the pugmill, and composite scrubbing liquor from the dust-recovery system (about 40-50% concentration) is added after being heated in a steam-jacketed vessel containing internal steam coils. An 11-55-0 grade ammonium polyphosphate (APP) can be produced using this process. The addition of highly concentrated (98.5% or greater) urea solution in essentially equal proportions to the APP melt permits production of 28-28-0 grade. Increasing the proportion of urea permits production of the 35-17-0 grade. Although moisture content of material in the pugmill is increased by the return of scrubbing liquor, only cooling is required to produce granules of good quality. The polyphosphate content of these products ranges from 15 to 35%, and the moisture content is usually 1% or less. A diatomaceous earth or kaolin clay conditioner is needed only for the 35-17-0 grade product. Typical operating conditions for the production of the three grades are shown in Table I.

Table I. Typical Operating Data for Melt Production and Granulation, TVA Demonstration Plant

Product grade	28-28-0	11-55-0	35-17-0
Production rate, mt/hr.	16	13	12
Urea			
75% solution			
Temp, °F (°C)	200 (93)	-	202 (94)
Feed rate (100% basis), mt/hr.	8	-	8
Melt to pugmill			
Temp, °F (°C)	285 (141)	-	290 (143)
Concentration, %	99	-	99
Ammonium polyphosphate			
Melt to pugmill, mt/hr.	8	13	4
Temp, °F (°C)			
Phosphoric acid	130 (54)	140 (60)	-
Anhydrous ammonia	100 (38)	78 (26)	-
Spray-reactor product	266 (130)	265 (129)	255 (124)
Pipe-reactor melt	422 (217)	420 (216)	412 (211)
pH			
Spray-reactor product	1.5	1.4	1.7
Pipe-reactor melt	3.4	3.5	4.1
Granulation			
Recycle			
Temp, °F (°C)	140 (60)	128 (53)	-
Ratio, kg/kg product	4.5	4.5	4.5
Granulator product			
Temp, °F (°C)	178 (81)	172 (78)	172 (78)
Screen analysis (Tyler), %			
+6 mesh	14	24	-
-6 +10 mesh	42	28	-
-10 +16 mesh	29	36	-
-16 mesh	15	12	-
Rotary coolers			
Temp, °F (°C)			
Recycle cooler	140 (60)	128 (53)	-
Product cooler	115 (46)	105 (41)	-
Product			
Chemical analysis, %			
Total N	28.7	11.1	35.5
Total P_2O_5	28.6	55.3	17.0
Available P_2O_5	28.6	55.2	-
Orthophosphate P_2O_5	23.2	45.6	11.4
Polyphosphate, % of total P_2O_5	18.9	17.5	32.9
H_2O (Karl Fischer)	1.0	1.1	0.8
Biuret	0.5	-	-
pH	4.9	3.6	-
Screen analysis (Tyler), %			
+6 mesh	2	2	1
-6 +8 mesh	28	33	22
-8 +10 mesh	52	45	53
-10 +12 mesh	10	11	20
-12 +16 mesh	7	8	3
-16 mesh	1	1	1

Use of this process, which does not require a rotary dryer and related equipment, would substantially reduce both capital and operating costs. A previous study (11) showed that battery limits plant cost for this melt-type granulation process was 20 to 25% less than that for conventional processes and that the total savings in production costs was $2 per metric ton for 11-55-0 grade and $3 for a 19-19-19 grade. A more recent cost estimate (12) showed that the plant investment for a melt-type granulation process for 11-55-0 grade ammonium phosphate (AP) was 15% less than that for conventional DAP processes and that the total savings in production costs was $2 per metric ton of 11-55-0 AP.

Pipe-Reactor/Drum-Granulator Process

Before 1974, all TVA studies involving melt granulation were conducted using a pugmill as the granulator to ensure proper mixing of the APP melt with recycled and feed solids. In 1974, TVA demonstrated the use of a drum granulator in a melt-type process on a pilot-plant scale (13). This process using a pipe reactor and drum granulator has the potential for eliminating the need for dryers in fertilizer plants equipped with conventional TVA ammoniator-granulators. Studies of this process have shown that good granulation can be obtained without the mixing action of a pugmill by discharging the melt from the pipe reactor directly into a drum granulator. This was accomplished by adding a section of perforated pipe to the discharge end of the pipe reactor (see Fig. 3 and 4). The melt is atomized by the steam that expands when released through the holes in the pipe. The holes are in a single straight line and are directed toward the bed of solids in the drum granulator. The size and number of holes are adjusted so that a pressure of 10 to 15 psig (0.70-1.06 kg/cm^2) is maintained in the pipe and good melt distribution is obtained. The perforated pipe also eliminates the need for a rotary vapor disengager such as that required in the pipe-reactor/pugmill process. The perforated pipe probably could be used with other types of granulators such as a pugmill or a pan granulator. Several NP and NPK grades have been produced in pilot-plant studies of this process using a preneutralizer, and MAP has been produced both with and without the use of a preneutralizer. Preneutralization was initially thought necessary to decrease scale formation in the pipe reactor. Later work indicated that a preneutralizer was not required to control scale formation in the pipe reactor.

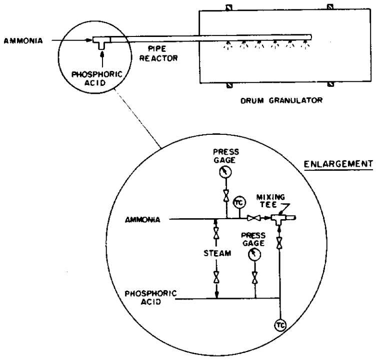


Figure 3. Configuration of Pilot-Plant Pipe Reactor

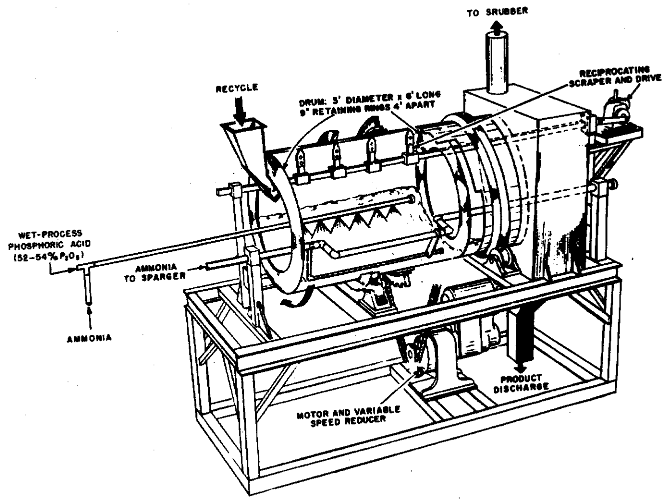


Figure 4. Pilot-Plant Pipe Reactor and Drum Granulator

Operation Using a Preneutralizer

In the pipe-reactor/drum-granulator process using a preneutralizer (see Fig. 5), merchant-grade (52-54% P_2O_5) wet-process phosphoric acid is heated to about 160°F (71°C) in the feed tank and recirculated through a scrubber to remove the free ammonia and dust from the granulator exhaust stream. A side stream of the recirculating acid is heated to 200°F (93°C) and metered to the preneutralizer tank with gaseous anhydrous ammonia to produce a slurry with an NH_3:H_3PO_4 mole ratio of about 0.4 and with a temperature of 280° to 300°F (138°-149°C). The pH of the slurry when diluted with water to a 10% solution by weight is about 1.8. About 40 to 50% of the free water in the feed acid is evaporated in the preneutralizer.

The partially ammoniated acid and enough additional ammonia are fed to the pipe reactor to produce a melt with an NH_3:H_3PO_4 mole ratio of about 1.05 and a temperature of 405° to 440°F (207°-227°C). Ammonia evolved from the granulator is about 5% of the total amount fed to the process under these conditions. Higher melt mole ratios are not feasible because of high vapor pressure and resulting loss of ammonia at the temperature in the pipe reactor. The melt is distributed through the perforated pipe onto the bed of solids in the drum granulator. For the 11-55-0 grade these solids consist only of the recycled material from the screening step. When producing NPK grades, urea prills and potassium chloride are added at metered rates to the recycle stream before it enters the drum granulator. When urea is fed in solid form, it can be better incorporated when it is added as microprills or as regular prills or granules crushed in a roll crusher. In these tests of NPK grades,

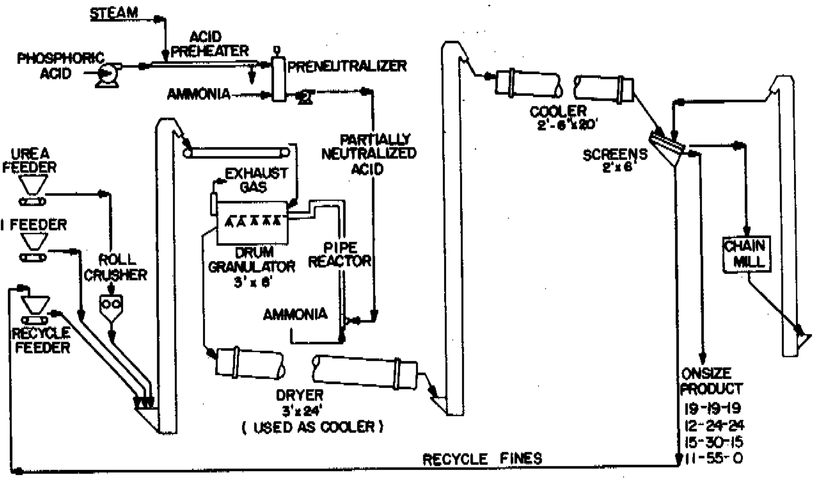


Figure 5. Pipe-Reactor/Drum-Granulator Process
Using a Preneutralizer

additional ammonia is added to the granulator to produce a product with an $NH_3:H_3PO_4$ mole ratio of about 1.3. The granules are cooled in a rotary cooler before they are screened. The rotary dryer, which was installed for another process, is not heated and serves as a cooler. Dry cyclones remove dust from the airstreams leaving the rotary vessels. In a commercial installation, only one cooler would be required, and either a system of bag filters or wet scrubbers would be used for dust removal. Oversize granules are crushed in a chain mill and rescreened. The undersize and sometimes part of the onsize are recycled to the granulator. Additional data from typical tests are given in Table II.

Fluorine evolved from the acid in the scrubber varies from 0.2 to 0.4 pound per ton of P_2O_5 (0.1-0.2 g/kg). Fluorine evolved from the preneutralizer tank varies from 0.2 to 4.4 pounds per ton of P_2O_5 (0.1-2.2 g/kg); from the granulator, it is only 0.03 pound per ton of P_2O_5 (0.015 g/kg). Scrubbing for removal of the fluorine compounds probably will be required to meet environmental emission standards from commercial-scale operations.

During operation of the pipe reactor, an iron aluminum ammonium orthophosphate scale forms on the inside walls of the reaction tube. The thickness of the scale which builds up on the walls of the pipe varies with the source of the phosphoric acid. With most acids, the scale formation is slow. Usually, the scale can be softened (after stopping the acid feed) by passing a low flow of steam and ammonia through the pipe for about 20 minutes. The soft scale can then be jarred loose and removed. On a few occasions, scale formation has blocked the pipe after a few hours of operation.

The plant investment and operating costs for the pipe-reactor/drum-granulator process using a preneutralizer would be about the same as for the pipe-reactor/pugmill process; however, energy requirements would be somewhat lower for processes using the rotary drum granulator because the drive horsepower required is less than that for a pugmill (11).

Table II. Formulations and Operating Conditions for Production of NP and NPK Fertilizers by Pipe-Reactor/Drum-Granulator Process

	19-19-19	12-24-24	15-30-15	11-55-0[b]	11-55-0[c]
Preneutralizer used	Yes	Yes	Yes	Yes	No
Formulation, lb/ton of product (kg/mt)					
Ammonia (gaseous)					
To preneutralizer	36 (18)	46 (23)	57 (28)	106 (53)	-
To pipe reactor	60 (30)	75 (38)	94 (47)	164 (82)	266 (133)
To drum	22 (11)	29 (14)	36 (18)	-	-
Total	118 (59)	150 (75)	187 (94)	270 (135)	266 (133)
Wet-process phosphoric acid (54% P_2O_5)	704 (352)	889 (444)	1111 (556)	2074 (1037)	2074 (1037)
Urea (46% N)	615 (308)	252 (126)	317 (158)	-	-
Potassium chloride (60% K_2O)	633 (316)	800 (400)	500 (250)	-	-
Preneutralizer					
Acid preheat temp, °F (°C)	210 (99)	180 (82)	200 (93)	190 (88)	-
Slurry temp, °F (°C)	293 (145)	290 (143)	282 (139)	279 (137)	-
NH_3:H_3PO_4 mole ratio	0.4	0.4	0.4	0.5	-
Pipe reactor					
Melt temp, °F (°C)	432 (222)	440 (227)	435 (224)	399 (204)	409 (210)
Melt analysis, %					
Total N	11.8	11.6	12.2	11.3	10.9
Total P_2O_5	57.8	58.0	57.2	56.3	57.3
Polyphosphate, as a % of total P_2O_5	20	21	21	10	11
Drum granulator					
Recycle ratio, kg/kg product	1.7	2.3	3.3	2.4	2.1
Product temp, °F (°C)	172 (78)	178 (81)	175 (79)	190 (88)	214 (101)
Moisture content, % AOAC (vacuum desiccation)	1.2	1.2	1.0	2.7	2.1
Screen analysis (Tyler), % retained					
6 mesh	4	33	22	39	33
8 mesh	14	62	40	61	55
10 mesh	35	84	58	76	71
12 mesh	52	91	68	84	79
16 mesh	83	97	83	93	91
Ammonia evolution, % of total feed	4	3	6	1	4
NH_3:H_3PO_4 mole ratio	1.3	1.3	1.4	1.1	1.0
Onsize (-6 +12 mesh) product analysis, %					
Total N	20.3	13.4	14.5	11.5	11.4
Total P_2O_5	20.1	25.1	29.6	55.0	55.7
K_2O[a]	19.8	24.3	18.6[a]	-	-
Percent of total P_2O_5 as					
Polyphosphate	27	23	20	7	5
Water soluble	94	99	100	94	95
Available	99	100	100	100	100
Moisture (AOAC vacuum desiccation)	1.1	1.2	0.9	2.1	1.4

---

[a] K_2O content high because sampling took place about 4 hours after changing from 12-24-24 grade.

[b] 122 kg/mt of water added to granulator as simulated scrubber solution.

[c] 115 kg/mt of water added to granulator as simulated scrubber solution.

Operation Without a Preneutralizer

Figure 6 shows a flowsheet of a modified version of the pipe-reactor/drum-granulator process in which a preneutralizer is not used. This simplifies the process considerably because a major piece of equipment and its related piping, transfer and metering equipment, and scrubbing system are not needed. Table II shows the operating conditions for a typical test producing an 11-55-0 grade MAP using this process without a preneutralizer. The product compares favorably with that of the process using a preneutralizer, but operation of the plant is easier because the preneutralizer and its associated equipment, which are relatively difficult to operate, are not used. Also, eliminating the preneutralizer and its scrubber and associated equipment would decrease the investment cost.

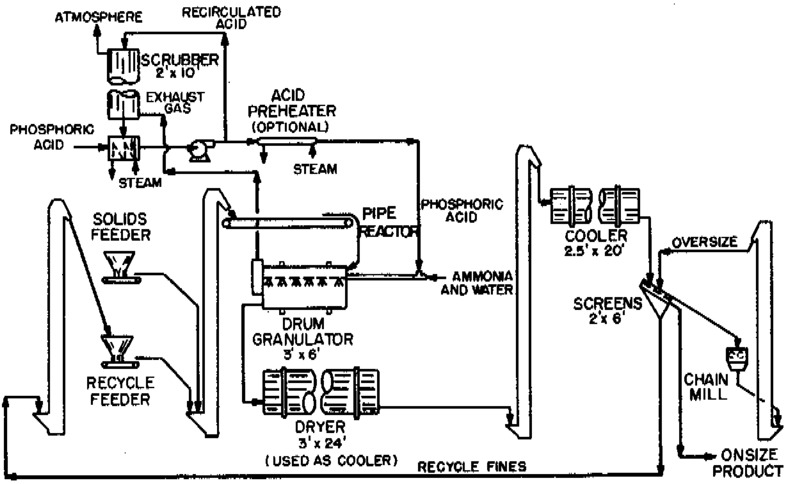


Figure 6. Pipe-Reactor/Drum-Granulator Process Without a Preneutralizer

In pilot-plant operations with the feed phosphoric acid preheated to 205°F (96°C) and with ammonia fed to the pipe reactor to give an $NH_3:H_3PO_4$ mole ratio of about 1.05, the temperature of the pipe-reactor melt is 400° to 420°F (204°-216°C). The melt contains 11 to 12% nitrogen and 56 to 58% total P_2O_5; about 10% of the P_2O_5 is in the polyphosphate form. Ammonia evolved from the granulator is about 4% of the total amount fed to the process, and about 96 to 99% of this is recovered in the acid recirculating through the scrubber. Acid at a temperature of about 160°F (71°C) is recirculated at a rate of about 5 gpm (18.9 l/min) through the 2- by 10-foot (0.61- x 3.05-m) packed-bed scrubber. The acid is maintained at this temperature by the addition of supplemental heat in the acid feed tank to prevent condensation of the water vapor in the exhaust airstream from the granulator. As in the process using a preneutralizer, dry cyclones are used to remove dust from the exhaust streams of rotary coolers. In addition to the cyclones, a system of bag filters or wet scrubbers would be needed in commercial installations to meet emission regulations. The granulator exhaust could be scrubbed either with water or with feed acid as was done in pilot-plant tests. If acid scrubbing is used, an additional scrubber would be required to remove fluorine from the acid scrubber exhaust stream.

Pipe-Cross Reactor/Drum-Granulator Process

TVA has done considerable developmental work on a process that uses a modified pipe reactor in which a pipe cross is used instead of a pipe tee. This modified pipe reactor (pipe-cross reactor) allows large quantities of both phosphoric and sulfuric acid to be used in formulations and has many advantages over conventional processes involving ammoniation in a preneutralizer tank. The pipe-cross reactor was developed in an effort to solve a pollution problem encountered in a TVA study of the incorporation of sodium nitrate into granular fertilizer. The sodium nitrate, which was a byproduct of a Defense Department operation, consisted of fine, moist crystals that were not suitable for direct application to the soil. Beginning in 1973, the Missouri Farmers Association (MFA) of Palmyra, Missouri, cooperated with TVA in conducting tests in their ammoniation-granulation plant. In early tests, the reacting sodium nitrate, sulfuric acid, and ammonia broke into flames in the granulator and emitted large volumes of brownish-white fumes. The addition of phosphoric acid did not suppress the flames and fuming. Thus, in an effort to overcome this problem, a pipe-cross reactor was installed in place of the preneutralizer. Although initial development of the pipe-cross reactor was in this commercial plant and several NP and NPK grades have been successfully produced there, TVA has continued pilot-plant studies of the pipe-cross reactor/drum-granulator process to further define process variables in an effort to improve the process and to produce a wider range of grades.

Advantages of Pipe-Cross Reactor

Some of the advantages of using the pipe-cross reactor instead of a preneutralizer in a conventional ammoniator-granulator plant are as follows:

1. Larger amounts of acid, both phosphoric and sulfuric, can be used in formulations.
2. Drying of the product is not normally required and fuel costs are lower.
3. There is less formation of troublesome ammonium chloride fume which is difficult to scrub from exhaust gases.
4. Investment costs are lower.
5. Operation of the plant is easier because preneutralizer slurry pumps, lines, meters, etc., are not required.
6. Moisture content of the slurry or melt produced is lower and there is a more favorable moisture balance in the process.
7. Granular MAP, which is an excellent product for blending, can be produced more conveniently; a wider range of grades can be blended with MAP (12-48-0 or 11-55-0) than with DAP (18-46-0).
8. Pollution control is easier and less expensive because the preneutralizer and its scrubbers are eliminated.

Commercial Plant Tests

The latest recommended design for a pipe-cross reactor for use in commercial plants is shown in Figure 7. Use of this 6-inch-diameter (15.2 cm) reactor tube allows high production rates while maintaining the optimum heat flux of 0.6 x 10^6 Btu/(hr.)(in.^{2} cross section) [23.4 x 10^6 cal/(hr.)(cm^2 cross section)] recommended in processes using granulators 10 by 20 feet (3.05 x 6.1 m) or smaller. Since its development 3 years ago, the pipe-cross reactor has been used in the production of a number of NP and NPK grades. These grades include 12-48-0, 6-24-24, 8-24-24, 12-12-12, 13-13-13, 8-22-11, 32-16-0, and 16-20-0. The production rates for these grades range from about 20 to 40 tons (18-36 mt) per hour. Tables III, IV, and V show production test results of 12-48-0-3.5S, 16-20-0-14S, and 32-16-0-3.6S, respectively.

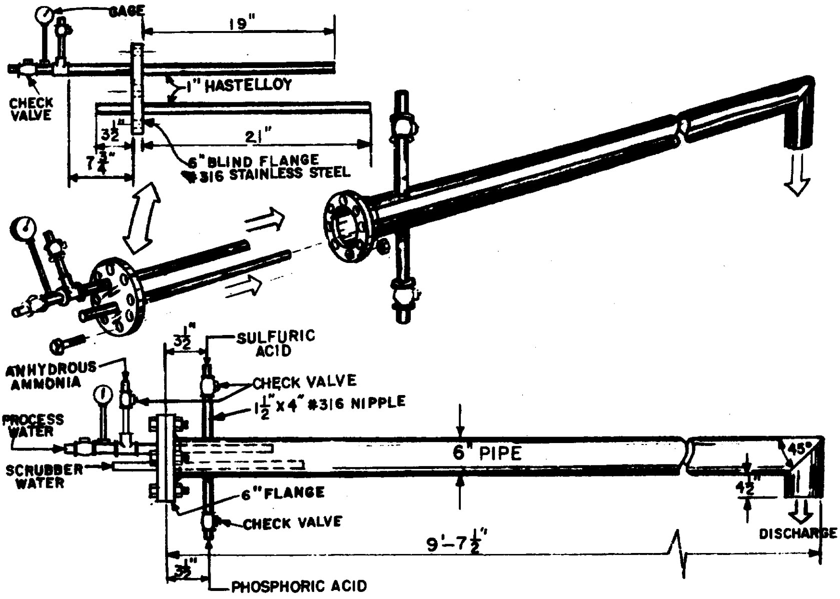


Figure 7. Latest Recommended Design of Pipe-Cross Reactor

Table III. Plant Test Data for Production of Granular Monoammonium Phosphate 12-48-0-3.6S with a 3-Inch Pipe-Cross Reactor

Formulation, lb/ton of product (kg/mt)	
Pipe-cross reactor (PCR)	
Ammonia	147 (74)
Sulfuric acid (93% H_2SO_4)	228 (114)
Phosphoric acid (54% P_2O_5)	600 (300)
Water	59 (30)
$NH_3:H_3PO_4$ mole ratio	0.95
Ammoniator-granulator	
Ammonia	146 (73)
Phosphoric acid (54% P_2O_5)	1265 (632)
$NH_3:H_3PO_4$ mole ratio	0.91
Duration of test, hr.	32
Operating results	
Production rate, tons/hr. (mt/hr.)	18 (16.3)
Recycle ratio, kg/kg product	3.8[a]
Granulator product, average pH	4.0
Average temp, °F (°C)	
Material from granulator	236 (113)
Dryer exit gas[b]	174 (79)
Product (estimated)	110 (43)
PCR heat flux, 10^6 Btu/(hr.)(in^2 cross section)	0.86
Total chemical heat, 10^3 Btu/ton (10^3 kcal/mt)	686 (191)
Total weight acid in formulation	
Lb/ton product (kg/mt)	2093 (1046)
Product	
Chemical analysis, %	
N	12.9
P_2O_5	46.7
H_2O[c]	1.2
Screen analysis (Tyler), %	
+6 mesh	0.8
-6 +8 mesh	48.3
-8 +12 mesh	50.6
-12 +14 mesh	0.3
-14 +16 mesh	0
-16 +20 mesh	0

---

[a] Calculated by measuring volume of material on recycle belt.

[b] Burner off during all these tests, dryer used as a cooler.

[c] Estimated by doubling the results of the rapid analysis method.

Table IV. Plant Test Data for Production of 16-20-0-14S with a 6-Inch Pipe-Cross Reactor

Dates (1977)	8/19-8/20	8/20-8/21
Operating time, hr.	9	25
Average production rate, tons/hr. (mt/hr.)	29 (26.3)	25 (22.7)
Formula No.	TVA-2-16-20	TVA-2-16-20
Formulation, lb/ton of product (kg/mt)		
Pipe-cross reactor (PCR)		
Ammonia	246 (123)	246 (123)
Sulfuric acid (98% H_2SO_4)	494 (247)	494 (247)
Phosphoric acid (52% P_2O_5)	627 (314)	627 (314)
Water	102 (51)	102 (51)
Granulator		
Ammonium sulfate	505 (252)	505 (252)
Phosphoric acid (52% P_2O_5)	158 (79)	158 (79)
Ammonia	20 (10)	20 (10)
Scrubber water	-	-
Operating results		
Phosphoric acid strength (% P_2O_5)		
PCR	46.3	52.0
Granulator	46.3	43-52
Temp, °F (°C)		
Dryer outlet gas	250 (121)	242 (117)
Product from granulator	214 (101)	220 (104)
PCR skin	263 (128)	281 (138)
Dryer gas	On and off	Off
Estimated recycle rate, kg/kg product	4	4
pH of granulator product	3.5-4.5	4.2
PCR heat flux, 10^6 Btu/(hr.)(in^2 cross section)	0.56	0.56
Total chemical heat, 10^3 Btu/ton (10^3kcal/mt)	670 (186)	670 (186)
Ammonia loss, % of total N	-	0.6-1.2
Opacity, % average	-	5.0
Average back pressure in reactor, psig (kg/cm^2)	50 (3.5)	50 (3.5)
Product		
Chemical analysis, % (average)		
N	15.8	15.9
P_2O_5	22.7	22.8
pH	-	-
Screen analysis (Tyler), %		
+4 mesh	0	-
-4 +8 mesh	57.5	40.7
-8 +16 mesh	42.4	59.0
-16 mesh	0.1	0.3

Table V. Plant Test Data for Production of 32-16-0-3.6S with a 6-Inch Pipe-Cross Reactor

Date	8/24/77
Operating time, hr.	4
Average production rate, tons/hr. (mt/hr.)	20 (18.1)
Formula No.	TVA-2-32-16-0
Formulation, lb/ton of product (kg/mt)	
Pipe-cross reactor (PCR)	
Ammonia	172 (86)
Sulfuric acid (98% H_2SO_4)	225 (112)
Phosphoric acid (52% P_2O_5)	598 (299)
Water	65 (32)
Granulator	
Urea	1097 (548)
Operating results	
Phosphoric acid strength (PCR), % P_2O_5	53
Average temp, °F (°C)	
Dryer outlet gas	178 (81)
Product from granulator	185 (85)
PCR skin	270 (132)
Dryer gas	On
Estimated recycle rate, kg/kg product	4-5
pH of granulator product	6.0
PCR heat flux, 10^6 Btu/(hr.)(in.^{2} cross section)	0.30
Total chemical heat, 10^3 Btu/ton (10^3 kcal/mt)	417 (116)
Ammonia loss, kg/hr.	159[a]
Opacity, % average	25[a]
Average back pressure in reactor, psig (kg/cm^2)	35 (2.5)
Product	
Chemical analysis, % (average)	
Nitrogen	
NH_3-N	6.9
Urea-N	24.2
Total	31.1
P_2O_5	16.4
H_2O	0.6
pH	5.1

---

[a] Scrubber water circulation greatly reduced by line plugging. In a very brief test run the day before, ammonia loss was 9 kg/hr., opacity about 5%.

The following design factors have been found to be important.

1. The reactor should have a heat flux of 0.3×10^6 to 1.0×10^6 Btu/(hr.)(in.^{2} cross section) /11.72 $\times 10^6$ to 39.1×10^6 cal/(hr.)(cm^2 cross section)/.

2. The ratio of length of reaction tube to diameter should be between 18 and 24. Most tests were conducted with a ratio of about 22.

3. Water must be fed to the reactor with liquid ammonia, but it is not required with gaseous ammonia. The usual $H_2O:NH_3$ weight ratio of the feed to the reactor was 0.3; however, ratios as low as 0.05 and as high as 1.0 have been used successfully. Water addition is varied to control the exit temperature of slurry from the reactor, which in turn partially controls the loss of ammonia. Ammonia loss also depends on the $NH_3:H_3PO_4$ mole ratio of the slurry.

4. The point at which hot aqua ammonia is introduced into the reaction tube is critical. If it is too close to the acid inlet, there is a tendency for vibration to occur, and if it discharges too far down the reaction tube, there appears to be excessive ammonia loss. Best results have been obtained when the hot aqua ammonia discharges into the reaction tube at a point about 15 to 16 inches (38-41 cm) from the end of the cross. Also, the centerline of the ammonia pipe should be on or slightly above the centerline of the reaction tube.

5. The length of the hot aqua ammonia tube should be between 20 and 30% of the total length of the reactor. This is necessary for complete mixing of the water and ammonia prior to entry into the reaction tube.

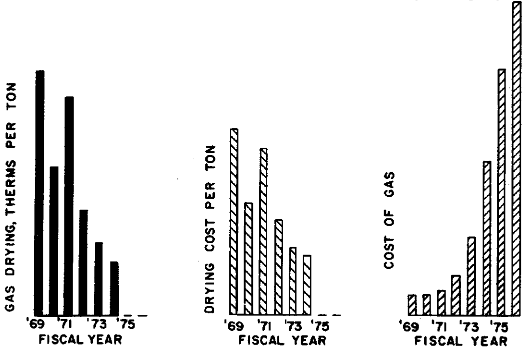
6. The reaction tube should be constructed of Hastelloy C-276 or C-4 pipe. Plant tests show that both Type 316 and Type 317 stainless steel reaction tubes failed after production of only about 2000 tons (1814 mt) of material.

The plant test data in Table III were obtained in production tests of an earlier design, 3-inch-diameter (7.6-cm) pipe-cross reactor. The 12-48-0-3.6S grade was produced because it blends easily with granular potash to produce a 6-24-24 blend. Blends made with the 12-48-0-3.6S grade are less subject to segregation in handling and application than blends made using ammonium nitrate, granular triple superphosphate, and potash. When all the sulfuric acid and 32% of the total phosphoric acid were fed to the pipe-cross reactor, an average production rate of about 18 tons (16.4 mt) per hour was maintained in the plant. The average throughput capacity of the plant was about 68 metric tons per hour. The average recycle rate was 3.8 tons of recycle per ton of product, which is about 25% less than the average recycle rate in a conventional DAP plant. The pipe-cross reactor heat flux was 0.9×10^6 Btu/(hr.)(in.^{2} cross section) /35.2 $\times 10^6$ cal/(hr.)(cm^2)/; the back pressure in the reactor was about 40 psig (2.8 kg/cm^2). Average temperature of the granulator product was 236°F (113°C) and the moisture content was about 2%. At this temperature and moisture, the dryer was used as an extra cooler and required no fuel. Average pH of the product was 4.0 indicating that almost all the phosphate was in the form of MAP.

Plant test data for the production of a 16-20-0-14S grade are included in Table IV. This grade, being high in nitrogen content, adapts very well to the pipe-cross reactor process. The total chemical heat in the formulation was about 670 x 10^3 Btu/ton (186 x 10^3 kcal/mt). The pipe-cross reactor heat flux was about 0.6 x 10^6 Btu/(hr.)(in.^{2} cross section) [23.4 x 10^6 cal/(hr.)(cm^2 cross section)]. As the operating results indicate, acid containing as low as 43% P_2O_5 was used. In a brief run before these two tests, 43% P_2O_5 acid was fed to the pipe-cross reactor and 28% P_2O_5 acid was added to the bed of the granulator. The use of less concentrated phosphoric acid saves energy. Also, the ammoniator-granulator scrubber stack emissions were very low. Only about 1% of the ammonia fed to process was lost, and the stack emissions had an average opacity of 5%. Analyses of emission samples collected during tests of the pipe-cross reactor/drum-granulator process in commercial plants have consistently shown that fluorine, chlorides, and particulate losses are very low. As indicated in the second 16-20-0-14S production run, no drying of the product was required.

The pipe-cross reactor/drum-granulator process has also been used with good success in the production of UAP sulfate (32-16-0-3.6S) grade fertilizers (Table V). This formulation contained almost 1100 pounds of urea per ton of product (550 kg/mt) and has proved somewhat difficult to make in a conventional preneutralizer/drum-granulator process because grades containing urea are difficult to dry. The production of this grade would require a small amount of drying to prevent buildup in rotary equipment and blinding of the screens. Although during this particular test the scrubber recirculation line plugged giving high emissions, a brief preliminary test with the scrubber operating properly showed very low ammonia losses with stack opacity of about 5%.

The great interest in this pipe-cross reactor/drum-granulator process is due to both reduced atmospheric emissions and energy savings in the elimination of drying for most grades. The MFA granulation plant, where this process was originally developed, has kept complete records of the natural gas consumption for fertilizer drying. A graph of their gas consumption records is shown in Figure 8. For the past 3 years, the MFA



METHOD OF OPERATION

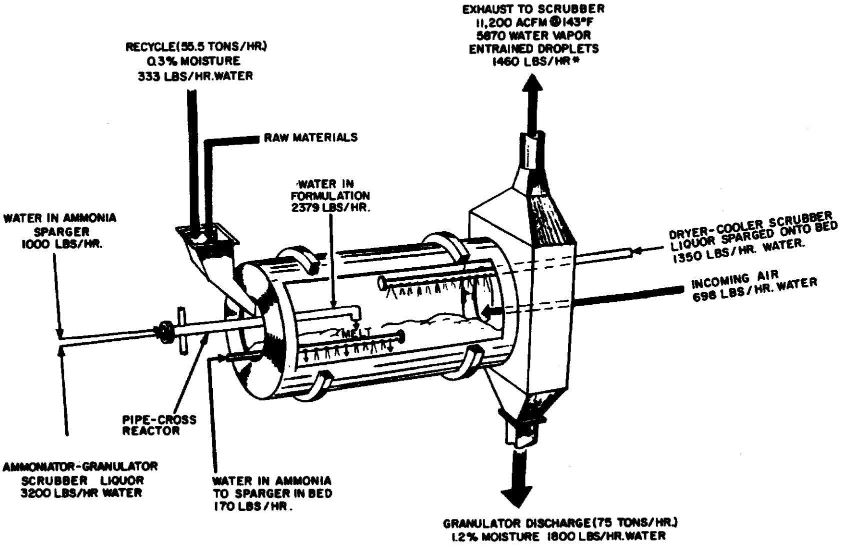
'72,'73,'74
USE OF SOME SUPERPHOSPHORIC ACID AND CHANGED OPERATIONS FROM A 1.4 MOLE RATIO TO 1.0

'74
BEGAN USE OF TVA PIPE-CROSS REACTOR

'75,'76
FULL USE OF PCR-- NO HEAT USED IN FERTILIZER PRODUCTION OTHER THAN THE HEAT OF REACTION OF THE CHEMICALS THEMSELVES.

Figure 8. Natural Gas Consumption and Costs for Drying Fertilizer Produced Using Pipe-Cross Reactor

plant has used no gas drying at all in the production of such grades as 12-12-12, 6-24-24, 8-22-11, and 12-48-0. In this plant, a water balance was obtained around the ammoniator-granulator during the production of 12-12-12 at a rate of 19.5 tons (17.7 mt) per hour. The results of this balance are shown in Figure 9. Adequate airflow through the granulator to carry off the evaporated water is very important in the process. As a general rule, granulation plants that are operating in the range of 20 to 30 tons per hour (18-27 mt/hr.) of product should have about 12,000 acfm (340 m^3/min) at about 140°F (60°C). Tests in granulation plants have been made with airflows that were too low to carry the moisture out of the granulator, and poor results were obtained. With the proper airflow and a formulation that contains a total chemical heat of 400 x 10^3 to 700 x 10^3 Btu/ton (111 x 10^3 to 195 x 10^3 kcal/mt), the flow of scrubber liquor to the pipe-cross reactor and to the bed of the granulator can be adjusted to control the granulator temperature and the quality of the fertilizer granules.



NOTE:
*CALCULATED FOR CLOSURE OF BALANCE, EMISSION TEST INDICATED THAT ACTUAL WATER CONTENT WAS 25.9% ADDITIONAL WATER AS ENTRAINED DROPLETS (1522 LBS/HR)

Figure 9. Water Balance Around Ammoniator-Granulator MFA, Palmyra Plant Test No. MFA-5-5-77 (Production Rate 19.5 Tons/Hour of 12-12-12)

Table VI. Formulations and Typical Operating Conditions for Production of NP Fertilizers Using the Pipe-Cross Reactor and Drum-Granulation Process

Nominal grade	12-48-0	12-48-0	33-11-0[a]	33-11-0[b]	33-11-0[c]	33-11-0[d]	18-46-0	18-46-0[e]	18-46-0[e]
Test No.	PCX 1-4	PCX-44	PCU-30	PCU-38	PCU-43	PCU-45	PCX-38	PCX-61	PCX-83
Length of test, hr.	17.0	5.0	5.1	5.8	5.5	5.0	5.4	5.8	6.1
Nominal production rate, mt/hr.	0.45	0.50	0.45	0.45	0.45	0.45	0.32	0.55	0.40
Formulation, lb/ton of product (kg/mt)									
Ammonia									
To pipe-cross reactor	292 (146)[f]	224 (112)[g]	96 (48)[f]	136 (68)[f]	96 (48)[f]	96 (48)[f]	330 (165)[g]	300 (150)[f]	300 (150)[f]
To granulator[f]	-	81 (40)	21 (10)	29 (14)	27 (14)	27 (14)	129 (64)	117 (58)	137 (68)
Ammonium sulfate (20.7% N)	-	-	165 (82)	-	-	-	-	-	-
Wet-process phosphoric acid (54% P_2O_5)									
To pipe-cross reactor	1778 (889)	1156 (578)	411 (206)	411 (206)	411 (206)	411 (206)	1721 (860)	1721 (860)	1721 (860)
To granulator	-	622 (311)	-	-	-	-	-	-	-
Sulfuric acid to pipe-cross reactor (92% H_2SO_4)	228 (114)	228 (114)	200 (100)	200 (100)	200 (100)	200 (100)	91 (46)	-	-
Urea (46% N)	-	-	1217 (608)	1183 (592)	1259 (628)	1259 (628)	-	-	-
Pipe-cross reactor									
Phosphoric acid feed temp, °F (°C)	158 (70)	151 (66)	152 (67)	153 (67)	155 (68)	155 (68)	155 (68)	155 (68)	121 (49)
Equivalent acid concentration, % P_2O_5	-	48	40	41	47	39	46	45	41
Ammonia feed temp, °F (°C)	Ambient	26 (-3)	Ambient	Ambient	Ambient	Ambient	25 (-4)	Ambient	Ambient
Melt temp, °F (°C)	431 (222)	248 (120)	269 (132)	278 (137)	276 (136)	264 (129)	240 (116)	290 (143)	264 (129)
Melt analysis, %									
Total N	11.5	12.4	11.3	16.8	37.0	13.0	13.6	15.0	12.4
Total P_2O_5	48.6	46.5	36.6	13.2	10.5	30.8	44.0	35.4	45.6
$NH_3:H_3PO_4$ mole ratio	0.98	0.85	0.46	1.46	-	0.67	1.32	1.40	1.38
Drum granulator									
Recycle ratio, kg/kg product	2.8	4.4	3.8	3.9	3.6	3.5	4.1	4.0	3.0
Discharge temp, °F (°C)	244 (118)	200 (93)	170 (77)	179 (82)	175 (79)	186 (86)	190 (88)	202 (94)	193 (89)
Moisture (AOAC), %	0.9	2.0	1.2	1.3	1.0	1.3	2.5	2.1	3.1
Screen analysis (Tyler), %									
+6 mesh	23.1	16.3	23.5	12.1	10.7	7.1	1.9	7.9	4.5
-6 +10 mesh	46.8	71.1	31.9	49.8	34.5	45.0	81.6	77.1	80.9
-10 +16 mesh	19.3	11.9	29.6	27.4	31.7	37.4	16.1	12.8	14.1
-16 mesh	10.8	0.7	15.0	10.7	23.1	10.5	0.4	2.2	0.5
NH_3 evolution, as % of total NH_3 feed	2.6	1.0	5.2	21.2	17.2	7.0	14.2	20.7	5.9
pH of granulator product	3.1	3.8	6.2	6.6	6.9	6.5	7.5	7.5	7.4
Onsize product									
Total N	12.0	12.3	33.9	34.6	36.4	35.6	18.2	18.1	17.8
Total P_2O_5	49.8	47.6	11.5	12.3	11.9	11.9	46.5	48.7	46.5
SO_3	9.7	10.4	14.0	10.3	8.5	8.6	5.3	-	-
As % of total P_2O_5									
Polyphosphate	7.4	0.4	10.9	5.7	10.9	11.8	1.5	1.0	-
Water soluble	93.2	91.4	91.3	93.5	92.4	94.1	87.2	86.4	92.5
Available	99.4	99.4	97.4	100	100	100	100	97.7	99.8
Moisture (AOAC)	0.8	1.4	0.8	1.4	0.8	0.9	2.3	1.9	2.6

---

[a] Five percent sulfur; ammonium sulfate added to bed; monoammonium phosphate mole ratio formulation.

[b] Three percent sulfur; diammonium phosphate mole ratio formulation.

[c] Three percent sulfur; urea added to the pipe cross; monoammonium phosphate mole ratio formulation.

[d] Three percent sulfur; monoammonium phosphate mole ratio formulation

[e] No sulfuric acid used in this formulation.

[f] Gaseous ammonia.

[g] Liquid ammonia.

Table VII. Formulations and Typical Operating Conditions for Production of NPK Fertilizers Using the Pipe-Cross Reactor and Drum-Granulation Process

Nominal grade	6-24-24	6-24-24	10-40-10	13-13-13	13-13-13	13-13-13	17-17-17	20-10-10
Test No.	PCX 11-12	PCX-18	PCX-5	PCX-40	PCX 6,9-10	PCX 13-15	PCHA-8	PCHA-6
Length of test, hr.	9.3	4.7	3.8	5.0	14.3	14.0	5.4	6.0
Nominal production rate, mt/hr.	0.91	0.91	0.45	0.68	0.55	0.68	0.68	0.68
Formulation, lb/ton of product (kg/mt)								
Ammonia								
To pipe-cross reactor	150 (75)[a]	101 (50)[a]	243 (122)[a]	187 (94)[b]	219 (110)[a]	187 (94)[a]	161 (80)[b]	144 (72)[b]
To granulator	-	50	-	32 (16)	-	32 (16)	-	-
Ammonium sulfate (20.7% N)	-	-	-	425 (212)	425 (212)	425 (212)	-	601 (300)
Wet-process phosphoric acid (54% P_2O_5)								
To pipe-cross reactor	863 (432)	548 (274)	1480 (740)	244 (122)	506 (253)	254 (127)	630 (315)	370 (185)
To granulator	-	296 (148)	-	244 (122)	-	254 (127)	-	-
Sulfuric acid to pipe-cross reactor (92% H_2SO_4)	91 (46)	103 (52)	189 (94)	480 (240)	480 (240)	486 (243)	250 (125)	300 (150)
Urea (46% N)[c]	-	-	-	-	-	-	448 (224)	340 (170)
Normal superphosphate	240 (120)	230 (115)	-	-	-	-	-	-
Potassium chloride (60% K_2O)	800 (400)	800 (400)	333 (166)	433 (216)	433 (216)	433 (216)	567 (284)	333 (166)
Pipe-cross reactor								
Phosphoric acid feed temp, °F (°C)	154 (68)	164 (73)	158 (70)	155 (68)	149 (65)	140 (60)	155 (68)	160 (71)
Equivalent acid concentration, % P_2O_5	-	-	-	46	-	-	50	44
Ammonia feed temp, °F (°C)	Ambient	Ambient	Ambient	33 (1)	Ambient	Ambient	22 (-6)	20 (-7)
Melt temp, °F (°C)	430 (221)	470 (243)	435 (224)	306 (152)	505 (263)[d]	517 (269)[d]	290 (143)	240 (116)
Melt analysis, %								
Total N	12.1	12.2	11.9	16.0	14.7	16.0	15.0	16.4
Total P_2O_5	48.4	46.1	48.1	12.9	29.3	17.1	35.4	28.0
$NH_3:H_3PO_4$ mole ratio	0.87	0.75	0.79	-	-	-	0.84	1.0
Drum granulator								
Recycle ratio, kg/kg product	1.0	1.7	2.8	1.6	2.3	1.6	3.8	3.4
Discharge temp, °F (°C)	207 (97)	210 (99)	207 (97)	223 (106)	230 (110)	226 (108)	166 (74)	158 (70)
Moisture (AOAC), %	3.2	2.5	2.7	1.5	0.7	1.6	1.1	0.9
Screen analysis (Tyler), %								
+6 mesh	29.4	17.1	11.8	19.8	37.0	39.4	12.3	10.0
-6 +10 mesh	30.1	54.3	50.7	29.7	30.7	39.4	36.6	32.2
-10 +16 mesh	27.3	23.5	30.7	37.6	19.7	18.3	33.8	32.2
-16 mesh	13.2	5.1	6.8	12.9	12.6	2.9	17.3	25.6
NH_3 evolution, as % of total NH_3 feed	2.4	5.0	2.3	20.0	11.4	9.3	16.9	11.2
pH of granulator product	4.3	4.2	3.2	4.3	4.2	4.3	5.8	5.2
Onsize product								
Total N	6.9	6.4	11.1	13.1	13.8	13.5	17.4	19.8
Total P_2O_5	26.1	24.5	42.3	13.3	16.8	14.8	17.5	10.4
K_2O	22.0	26.1	6.7	16.1	11.8	14.0	17.1	10.8
SO_3	9.1	8.4	10.2	29.8	30.6	30.5	14.1	29.0
As % total P_2O_5								
Polyphosphate	9.2	21.2	6.9	9.0	29.6	19.7	10.6	16.8
Water soluble	89.1	84.9	94.1	91.7	93.6	92.0	90.6	92.8
Available	100	100	99.8	99.2	100	98.6	100	100
Moisture (AOAC), %	2.4	1.6	1.8	1.3	0.5	1.0	1.1	0.9

[a] Gaseous ammonia.
[b] Liquid ammonia.
[c] TVA pan granulated.
[d] Water added to control temperature.

Commercial Plant Tests

Currently, about 15 pipe-cross reactors are being used in granulation plants in the United States. Although most of these pipe-cross reactors discharge into conventional TVA ammoniator-granulators, two of the pipe-cross reactors discharge into pugmills. Field experience to date shows the importance of operating the pipe at 300°F (149°C) or less and maintaining adequate water feed to the pipe. One pipe-cross reactor was operated at a higher temperature while being fed small quantities of high-sludge phosphoric acid, large quantities of sulfuric acid, and an inadequate quantity of water; this pipe plugged and ruptured. The degree of corrosion and its relative part in the pipe rupture are unknown; however, this experience emphasizes that more research into formulations, materials of construction, and operating conditions must be done before it will be known if the pipe-cross reactor can be successfully operated at temperatures above 300°F (149°C) for sustained periods. Hastelloy C-276 is not recommended for sustained operation above this temperature. Until further data are available, recommendations are to always add water with the ammonia to the pipe-cross reactor to promote the reaction and to operate at a discharge temperature of 300°F (149°C) or less. Firms cooperating with TVA on this process continue to be very pleased with their product quality, energy savings, reduced pollution, and ease of operation.

Pilot-Plant Results

Although initial development of the pipe-cross reactor/drum-granulator process was done in a commercial plant, some operating variables were still unknown. TVA began pilot-plant testing of this process in October 1975 to further define the operating variables, to produce a wider range of grades, and to study the following items:

- Operating temperatures
- Minimum and maximum quantities of sulfuric acid
- Quantity of water required with liquid ammonia
- Amount of polyphosphate formed
- Relative amount of fumes and dust formed
- Effect of $NH_3:H_3PO_4$ mole ratio on melt or slurry
- Materials of construction for pipe-cross reactor
- Methods of distribution of melt or slurry
- Recycle ratios
- Production of UAP sulfates
- Acid strengths required

These items were studied and modifications and improvements to the equipment and process were made so that a wide variety of grades was satisfactorily produced.

A typical flowsheet of the process equipment is shown in Figure 10. Formulations and typical pilot-plant operating conditions for several of these grades are shown in Tables VI and VII. An existing conventional granulation pilot plant was modified for this process, so although two rotary vessels are shown in addition to the drum granulator, both of these vessels are used as coolers. Heat has been added to the dryer only in a few tests producing 18-46-0 (DAP) when dilute phosphoric acid (less than 40% P_2O_5) was fed to the pipe-cross reactor. It was necessary to dry that product to reduce the product moisture to 2%.

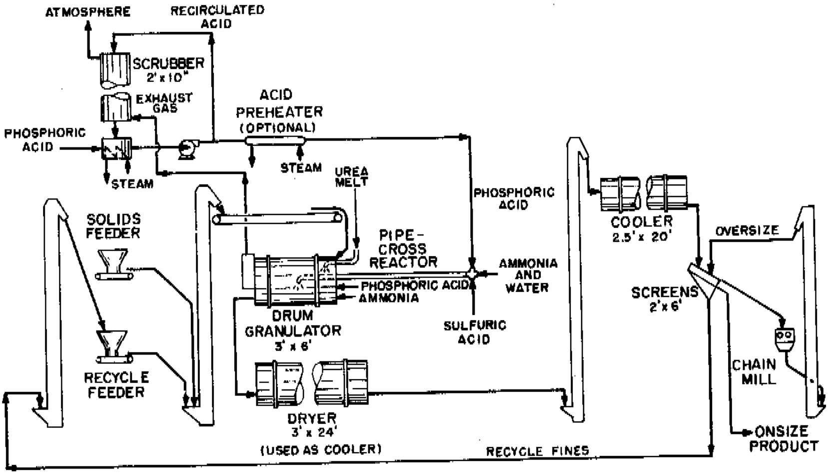


Figure 10. Pipe-Cross Reactor/Drum-Granulator Process

In the pipe-cross reactor/drum-granulator process, the feed wet-process phosphoric acid is recirculated at a rate of 3 to 5 gpm (11.4-18.9 l/min) through a 2- by 10-foot (0.61- x 3.05-m) packed-bed scrubber and heated to 140° to 160°F (60°-71°C) by the steam in the granulator exhaust and by the heat of reaction produced as the acid reacts with the free ammonia. A side stream of the recirculating acid is metered to the pipe-cross reactor. Enough ammonia is fed to the pipe to maintain the desired $NH_3:H_3PO_4$ mole ratio in the melt or low-moisture slurry produced. The temperature of the melt or low-moisture slurry is controlled either by adding water to the ammonia or by diluting the phosphoric acid to the desired concentration. The melt or low-moisture slurry is distributed through one of several types of distributors onto the rolling bed of solids in the drum granulator. In addition to the open-end, turned-down elbow shown in Figure 11, a slotted pipe and a pipe with two to four equally spaced drilled holes have been used as melt distributors. The actual distributor used depends on the requirements of the formulation being used. In pilot-plant scale, an even melt or slurry distribution is necessary because space is limited inside the relatively small granulator and small variations can produce large upsets in the system. Normally, drilled-pipe distributors are used when melts or slurries with a relatively high fluidity are produced, such as those of 18-46-0 with an $NH_3:H_3PO_4$ mole ratio of about 1.35 to 1.45 and 33-11-0 with a mole ratio of about 0.6 to 0.8. In other formulations with a melt or slurry mole ratio of about 1.0, a single-orifice distributor is usually a better choice.

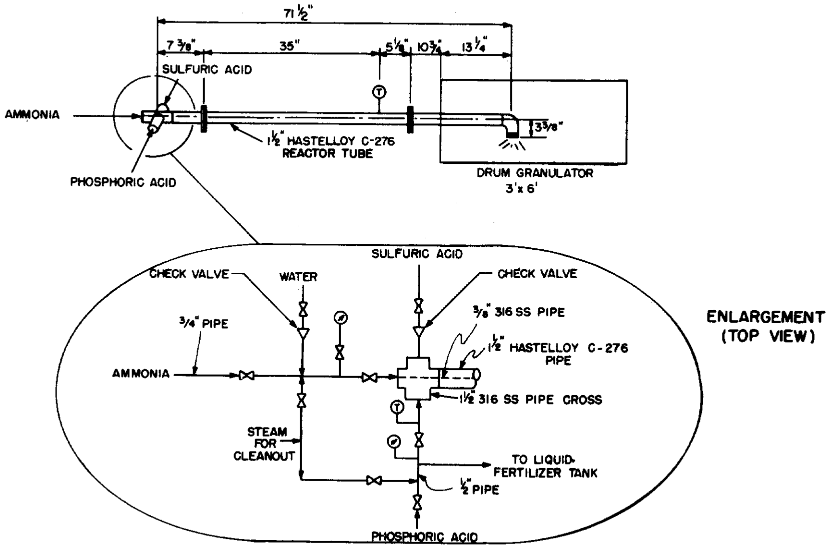


Figure 11. Configuration of TVA Pipe-Cross Reactor

A sketch of the first pipe-cross reactor used in the pilot-plant tests is shown in Figure 11. This reactor is composed of a 1-1/2-inch (3.81-cm) pipe cross made of Type 316 stainless steel. The reaction tube is 71-1/2 inches (182 cm) long and is made from 1-1/2-inch (3.81-cm) Schedule 40 Hastelloy C-276 pipe. A thermocouple well is installed in the reaction tube 42 inches (106.7 cm) downstream from the pipe cross. The acids are introduced into two opposite side arms of the pipe cross. The ammonia is introduced through the side arm opposite the reaction tube through a 1/4-inch (0.64-cm) or 3/8-inch (0.95-cm) Type 316 stainless steel pipe that extends through the pipe cross and about 2 inches into the reaction tube so that the violent acid neutralization reaction is confined to the reaction tube.

The original pipe-cross reactor was modified for later tests by replacing the 1-1/2-inch (3.81-cm) reaction tube with a 3/4-inch (1.90-cm) pipe. The first 3/4-inch (1.90-cm) reaction tube pipe was made of Type 316 stainless steel because Hastelloy C-276 pipe in that size was not readily available. However, two Type 316 stainless steel reaction tubes that were used operated an average of only 148 hours before each failed at a point about 12 inches (30.48 cm) downstream from the point of introduction of the ammonia. There has been no indication of severe corrosion of the 1-1/2-inch (3.81-cm) Hastelloy C-276 reaction tube after 273 hours of operation. It is recommended that the reaction tube be constructed of Hastelloy C-276 or Hastelloy C-4 pipe. The Type 316 stainless steel pipe cross has now been used for more than 670 hours without failure. The 1/2-inch (1.27-cm) threaded pipe nipple used to feed sulfuric acid into the pipe-cross reactor side arm lasted an average of only 97 hours before failure in the cold-worked threaded section. The last pipe nipple installed was welded and is in satisfactory condition after more than 360 hours of operation.

A total of eight grades has thus far been produced using the pipe-cross reactor, and two additional will be made this year. Of these eight grades, four were MAP sulfate grades, three were UAP sulfates, and one was DAP. In producing one of these three grades, urea melt could be fed either (1) along with the ammonia or the phosphoric acid to the pipe-cross reactor, (2) to the reactor reaction tube, or (3) sprayed onto the bed of solids in the granulator. Products with $NH_3:H_3PO_4$ mole ratios of 1.0 and 1.9 to 2.0 were produced. In the other two UAP sulfate grades, urea microprills were fed to the granulator along with the recycled solids.

The following observations were made of pipe-cross reactor operation during pilot-plant tests conducted to date.

- Sulfuric acid has been fed at rates up to 500 pounds per ton of product (250 kg/mt). Higher rates could have been fed if higher feed pressures were available.

- Best operation with less buildup occurred with operating temperatures below 300°F (149°C) or above 400°F (204°C). Materials of construction should be thoroughly investigated before sustained operations above 400°F (204°C) are made, especially if sulfuric acid is fed.

- Melt or slurry distribution can be improved by maintaining an $NH_3:H_3PO_4$ mole ratio in the pipe-cross reactor of about 0.6 to 0.8 for MAP formulations and 1.35 to 1.45 for DAP formulations.

- The pipe-cross reactor operated equally well with either liquid or gaseous ammonia feed. With liquid ammonia, at least 0.1 pound water per pound ammonia was fed along with the ammonia to maintain smooth operation and enhance ammonia retention.

- Buildup in the reaction tube was usually an amorphous iron aluminum ammonium orthophosphate scale when reaction temperatures were 400°F (204°C) and higher, but the buildup was usually a solidified melt or slurry product at lower temperatures. The buildup rate was strongly related to acid source.

- The buildup was formed in the first 12 inches (30.5 cm) of the reaction tube when DAP was produced without using sulfuric acid but occurred at the discharge end of the reaction tube when sulfuric acid was used.

- Ammonia evolution from the pipe-cross reactor was directly related to temperature and $NH_3:H_3PO_4$ mole ratio of the melt or slurry.

- Urea melt could be fed to the pipe-cross reactor either along with the ammonia or to the reactor tube; however, hydrolysis of the urea occurred with both and a very foamy pipe-cross reactor product was produced. Ammonia evolution from the granulator was higher than in tests where the urea melt was sprayed onto the bed of the granulator.

- In producing the 33-11-0 grade, it was possible to feed a simulated scrubber solution (40% by weight dust solution) along with the phosphoric acid feed to the pipe-cross reactor. The solution could not be added along with the ammonia because the reaction between the two would produce a blockage in the line after only 5 to 10 minutes of operation.

Recent pilot-plant tests have produced a 33-11-0 grade UAP sulfate. Previous tests were conducted to determine the best process conditions at which to produce this grade; later tests were made to determine how evolved dust could be returned to the system. In all these tests, dust from the rotary coolers was collected by cyclones and metered to the recycle stream. However, this was a minor source of dust evolution since 60 to 90% of the total dust is evolved at the miscellaneous dust pickup points (elevators, chutes, conveyors, screens, chain mill, etc.). Tests did show that the dust from the miscellaneous pickup points could be returned with the recycle without affecting granulation. Other tests were made with a 40% by weight dust solution being fed to the process to simulate return of dust from the miscellaneous dust pickup points. This solution was added to the phosphoric acid feedline of the pipe-cross reactor; however, no more than 40% of the evolved dust from the miscellaneous dust pickup points could be returned to the system. The dust solution was not successfully fed along with the ammonia to the pipe-cross reactor.

A DAP of an 18-46-0 grade has also been produced using the pipe-cross reactor. Tests have been made both with and without sulfuric acid fed to the pipe-cross reactor. The most recent series of 14 tests have used 37.5 to 42.5% P_2O_5 phosphoric acids and no sulfuric acid. The slurry was ammoniated to an $NH_3:H_3PO_4$ mole ratio of about 1.35 in the reactor and further ammoniated in the granulator to produce a product with a mole ratio of 1.9 to 2.0. Recycle ratios averaged 2.7. The average pipe-cross reactor and granulator discharge temperatures were 260°F (127°C) and 187°F (86°C), respectively. However, product moistures averaged about 3%, so some drying would be required to maintain a product moisture content consistently below 2%. Ammonia evolution from the granulator averaged 14.5% of the total ammonia fed to the process. The average fluorine evolution for these tests was 0.03 pound per ton of P_2O_5 (0.015 g/kg) from the granulator and 0.69 pound per ton of P_2O_5 (0.34 g/kg) from the acid scrubber.

Tests are currently being conducted to produce a 15-15-15 grade fertilizer using urea and to compare the relative drying costs of the conventional DAP process versus the pipe-cross reactor process. The pipe-cross reactor process producing DAP will be demonstrated at TVA's Twelfth Demonstration of Fertilizer Technology at Muscle Shoals, Alabama, on October 17-18, 1978.

REFERENCES

1. Houston, E. C., Hignett, T. P., and Dunn, R. E., Ind. Eng. Chem. 43, 2413-18 (October 1951) (TVA Reprint CD-136).

2. Membrillera, F. G., Toral, J. L., and Codina, F., "Use of MAP Slurry from a Pipe Reactor in Granular Fertilizer Production." (Paper presented at the International Conference on Granular Fertilizers and Their Production, London, England, November 13-15, 1977.)

3. Torney, J. G., "Manufacture of Granular Ammonium Phosphates Using a Pipe Reactor Process." (Paper presented at the Fertilizer Industry Round Table, Washington, DC, October 25-27, 1977.)

4. Lee, R. G., Meline, R. S., and Young, R. D., "Pilot-Plant Studies of an Anhydrous Melt Granulation Process for Ammonium Phosphate-Based Fertilizers," ISMA Proc., Paper No. 5, Sandefjord, Norway (September 8-11, 1970).

5. Lee, R. G., Meline, R. S., and Young, R. D., "Pilot-Plant Studies of Anhydrous Melt Granulation Process for Ammonium Phosphate-Based Fertilizers," Ind. Eng. Chem. PDD 11 (1), 90-4 (January 1971) TVA Reprint X-98).

6. Lee, R. G., Norton, M. M., and Graham, H. G., "Urea-Ammonium Phosphate Production Using the TVA Melt-Type Granulation Process," Proc. Fert. Ind. Round Table, 16 pp (December 1974).

7. Achorn, Frank P. and Balay, Hubert L., "Production of Granular Ammonium Phosphate Sulfate NPK Mixtures." (Paper presented at Annual Meeting of the Fertilizer Industry Round Table, Washington, DC, December 3-5, 1974.)

8. Achorn, Frank P., and Salladay, David G., "Production of Monoammonium Phosphate in a Pipe-Cross Reactor." (Paper presented at the 25th Annual Fertilizer Industry Round Table, Washington, DC, November 4-6, 1975.)

9. Achorn, Frank P., and Salladay, David G., "TVA's New Pipe-Cross Reactor Process for Granular Ammonium Phosphates." (Paper presented at the American Chemical Society Meeting, August 29 through September 3, 1976, San Francisco, California.)

10. Salladay, David G., and Myers, Edwin D., "The Use of TVA's Pipe-Cross Reactor to Conserve Energy in Fertilizer Granulation Plants." (Paper presented at the Fifth National Conference on Energy and the Environment, November 1-3, 1977, Cincinnati, Ohio.)

11. Young, Ronald D., and Lee, Robert G., "Advantages in Energy, Fuel, and Investment Savings by Melt-Type Granulation Processes." (Paper presented at the Technical Conference of International Superphosphate and Compound Manufacturers Association Limited, and The Fertilizer Association of India, December 8-10, 1975, New Delhi, India.) (TVA Reprint No. Z-70.)

12. "Cost Estimate—Ammonium Polyphosphate Versus Diammonium Phosphate." (Interoffice memorandum by F. E. Lancaster, Jr., to W. C. Scott, dated June 24, 1977, Tennessee Valley Authority, Division of Chemical Development, Process Engineering Branch, Muscle Shoals, Alabama 35660.)

13. "New Developments in Fertilizer Technology," Tennessee Valley Authority Bulletin Y-81. (10th Demonstration, October 1974, Muscle Shoals, Alabama).